



Accommodation coefficient of HOBr on deliquescent sodium bromide aerosol particles

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**Accommodation
coefficient of HOBr**

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Accommodation coefficient of HOBr on deliquescent sodium bromide aerosol particles

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Abstract

Uptake of HOBr on sea salt aerosol, sea salt brine or ice is believed to be a key process providing a source of photolabile bromine (Br₂) and sustaining ozone depletion cycles in the arctic troposphere. In the present study, uptake of HOBr on sodium bromide (NaBr) aerosol particles was investigated at an extremely low HOBr concentration of 300 cm⁻³ using the short-lived radioactive isotopes ⁸³⁻⁸⁶Br. Under these conditions, at maximum one HOBr molecule was taken up per particle. The rate of uptake was clearly limited by the mass accommodation coefficient, which was calculated to be 0.6±0.2. This value is a factor of 10 larger than estimates used in earlier models. The atmospheric implications are discussed using the box model "MOCCA", showing that the increase of the accommodation coefficient of HOBr by a factor of 10 only slightly affects net ozone loss, but significantly increases chlorine release.

1. Introduction

Ozone plays an important role in the chemistry and the radiation budget of the troposphere. In the polar troposphere, episodes with very low ozone levels have been observed in the past twenty years in the Arctic (Bottenheim et al., 1986; Galbally and Roy, 1980; Oltmans, 1981; Oltmans and Komhyr, 1986) and the Antarctic (Wessel et al., 1998). These episodes occur frequently between polar sunrise and early summer and cover extended areas over the arctic troposphere (Mickle, 1989). From the correlation between the sudden ozone loss events and the bromine content of the air mass (Barrie et al., 1988; Barrie et al., 1989) it was postulated that ozone is being depleted by reaction with the bromine radical, Br (Barrie et al., 1988; Bottenheim et al., 1990; Finlayson-Pitts et al., 1990; Langendörfer et al., 1999). The presence of BrO, the primary product of O₃ with Br, in the atmospheric boundary layer has been verified in situ during tropospheric ozone depletion events (Hausmann and Platt, 1994; Stutz et al., 1999; Tuckermann et al., 1997). Many suggestions have been made how sea salt

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bromide either in the sea salt aerosol or as brine on the sea ice surface could provide a source of photolabile Br₂ as a source of Br radicals to sustain ozone destruction (Fan and Jacob, 1992; Finlayson-Pitts et al., 1990; Langendörfer et al., 1999; Le Bras and Platt, 1995; McConnell et al., 1992; Mozurkewich, 1995; Tang and McConnell, 1996; Wessel et al., 1998). A very efficient way to release Br₂ into the gas-phase especially in the clean marine boundary layer is through autocatalytic cycles (Vogt et al., 1996) involving the reaction of HOBr with Bromide (Br⁻) in the sea salt solution,



and its analogue with chloride. The bulk liquid phase chemistry of reaction (1) has been explored by Eigen and Kustin (1962), and with respect to its significance to the marine boundary layer, Fickert et al. (1999) investigated the Br₂ and BrCl yield in the gas-phase for mixed bromide and chloride solutions as a function of pH. This chemistry is not restricted to the arctic boundary layer. In mid-latitudes at the Dead Sea, events with very high BrO concentrations were observed (Hebestreit et al., 1999), which were caused by bromine release from saltpans. In the sub-tropical North-western Pacific at Ogasawara Hahajima Island (Nagao et al., 1999) as well as in the mid-latitude South-west pacific at Cape Grim (Galbally et al., 2000) a distinct sunrise ozone destruction (SOD) was observed. It was speculated that this is due to halogen (esp. bromine) reactions. Based on model calculations, Von Glasow et al. (2001) explained the diurnal variation of BrO with a peak early in the morning, which could be the cause of the SOD.

A quantitative understanding of ozone chemistry in the marine boundary layer and its reliable modelling requires a more detailed knowledge of the processes governing HOBr uptake from the gas-phase and its reaction in the liquid phase. The kinetics of a heterogeneous process is commonly described in terms of the uptake coefficient, γ_{upt} , defined as the probability that a molecule undergoing a gas-kinetic collision with the particle surface is actually undergoing processing on or beyond this surface (Hanson et al., 1994). The flux of reactive molecules from the surrounding gas to the particle surface depends on the particle size and the value of γ_{upt} . Macroscopically, this is

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accounted for by expressing the first order loss rate coefficient k_g^l of $\text{HOBr}_{(g)}$ by

$$k_g^l = \gamma_{\text{net}} \cdot N_p \pi d_p^2 \cdot \frac{\nu}{4}, \quad (2)$$

where γ_{net} denotes the net uptake coefficient, N_p the number density of particles ($\#/\text{cm}^3$), d_p the particle diameter (cm), and ν the mean thermal velocity (cm/s). Within

5 this framework, γ_{net} can be expressed as

$$\frac{1}{\gamma_{\text{net}}} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{\gamma_{\text{upt}}}. \quad (3)$$

This notation indicates that the effect of diffusion to the particle surface is to add an additional resistance to uptake, and can also be understood as a correction to the purely gas-kinetic flux to the surface area. The smaller γ_{upt} and d_p , the smaller is the contribution of Γ_{diff} to k_g^l . For the particle size range that is most relevant to atmospheric chemistry, Fuchs and Sutugin (1970) have derived an approximation:

10

$$\frac{1}{\Gamma_{\text{diff}}} = \frac{0.75 + 0.28 Kn}{Kn(1 + Kn)} \quad (4)$$

with the Knudsen number defined as

$$Kn = \frac{6D}{\nu d_p}. \quad (5)$$

15

Along the same line as to include diffusion resistance, γ_{upt} is represented as a superposition of accommodation and loss within the bulk liquid due to reaction:

$$\frac{1}{\gamma_{\text{upt}}} = \frac{1}{\alpha} + \frac{1}{\Gamma_{\text{rxn}}} = \frac{1}{\alpha} + \frac{\nu}{4HRT\sqrt{k_{\text{aq}}^l D_{\text{aq}}}}, \quad (6)$$

where α denotes the accommodation coefficient, i.e., the probability that the molecule accommodates and dissolves in the vicinity of the surface, also commonly denoted as mass accommodation coefficient. Γ_{rxn} is the probability of reaction in the liquid phase.

20

H denotes the Henry's Law coefficient (HOBr: $>1.9 \times 10^3$ (Blatchley et al., 1992) and $6.1 \times 10^3 \text{ M atm}^{-1}$ (Frenzel et al., 1998), R the gas constant, D_{aq} the diffusion coefficient of HOBr in the liquid phase, and k_{aq}^{I} the first order loss rate constant of HOBr in the liquid phase.

5 Aside from two studies of HOBr uptake on bromide doped ice (Abbatt, 1994; Kirchner et al., 1997) data on the heterogeneous chemistry of reaction (1) are very scarce. In their modelling study, Sander and Crutzen (1996) used an estimated value of 0.056 for the accommodation coefficient, α , of HOBr on deliquescent sea-salt to calculate γ_{upt} as
 10 no experimental value was available. Mochida et al. (1998) found an upper limit for γ_{upt} of 0.18 on solid KBr, suggesting that this value also sets a lower limit to α , for, however, a dry bromide surface. Due to diffusion limitations of the experiment, Fickert et al. (1999) could only derive a lower estimate for α of 0.2, but on the other hand obtained an experimental value for the diffusion coefficient in the gas-phase, allowing a more reliable assessment of Γ_{diff} . Abbatt and Waschewsky (1998) for the first time measured
 15 the uptake coefficient of HOBr to deliquescent NaCl aerosols. On acidified NaCl, γ_{upt} was between 0.1 and 0.2, at the limit where under their experimental conditions γ_{upt} became controlled by diffusion, whereas on unbuffered NaCl γ_{upt} was about 10^{-3} , clearly due to consumption of the available acidity in the aerosol. From that study, again a lower limit to the accommodation coefficient of 0.2 has been suggested.

20 Therefore, a reliable measurement of the presumably high accommodation coefficient on deliquescent sea salt is still missing. The requirements for such an experiment are relatively strict: the uptake should not be limited by diffusion. Due to the high vapour pressure of water, the loss to the walls of a cylindrical flow tube remains diffusion limited. Therefore, an experiment with deliquescent particles in gas-suspension
 25 at atmospheric pressure is appropriate if the particle diameter is small enough so that $1/\Gamma_{\text{diff}}$ remains small, i.e. clearly in the sub-micron range. On the other hand, due to the extremely low aerosol mass in that size range, this implies that an appreciable processing of the particles (be it bromide or the acidity) occurs until measurable amounts of HOBr are lost from the gas-phase, so that the system becomes rapidly

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limited by one of the reactants, but not by the accommodation coefficient. One way out of this is by using a radioactive isotope. In previous studies using ^{13}N , the potential of this method to investigate the heterogeneous chemistry of nitrogen oxides at very low concentrations has been shown (Ammann, 2001; Ammann et al., 1998; Arens et al., 2001; Kalberer et al., 1999; Kalberer et al., 1996). Recently, an approach to generate short-lived bromine isotopes in defined chemical form in the gas-phase has been developed (Wachsmuth et al., 2001; Wachsmuth et al., 2000), based on a gas-jet facility mounted at the Swiss Spallation Neutron Source (SINQ) at Paul Scherrer Institute. In a campaign at this facility, reported here, $\text{HO}^{\text{A}}\text{Br}$ ($\text{A} = 83\text{--}86$) was allowed to react with deliquescent 100 nm-NaBr particles in gas suspension. The HOBr concentration of a few hundred molecules per cm^3 was so low, that the uptake was only limited by the accommodation coefficient and the acidity of the aerosol was not depleted.

2. Experimental

2.1. Generation of labelled HOBr

The system delivering short-lived bromine isotopes as gas-phase molecules has been described in detail elsewhere (Wachsmuth et al., 2001; Wachsmuth et al., 2000). Briefly, $\text{HO}^{83\text{--}86}\text{Br}$ was produced as following. At the Swiss Spallation Neutron Source (SINQ) at Paul Scherrer Institute (PSI), a small amount of ^{235}U was irradiated with thermal neutrons resulting in fission of ^{235}U and delivering several selenium isotopes (among many other nuclides), which were emitted into a carrier gas (5% O_2 in He, humidified to 10% relative humidity). The Se isotopes form selenous acid molecules, which were swept to the laboratory, where they were thermally decomposed to elemental selenium and probably SeO_2 and deposited on quartz at 130°C (see Fig. 1). The Se isotopes decay into their daughter bromine isotopes. This β^- decay, in which an electron with 1.4 MeV energy is emitted, certainly results in a highly excited Br^+ ion, the fate of which is not known in detail. As the bromine isotope could only be released

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from the quartz surface, when O_2 was added, we believe that the initial molecule might have been BrO or $OBrO$ which react to $HOBr$ in a second step. The large quartz surface also seemed to be essential possibly as substrate for H_2O adsorption providing a way for more efficient reaction of $OBrO$ with H_2O . Also, the electron emitted might have induced a high density of radicals (O , OH , HO_2) in the immediate vicinity of the bromine isotope promoting the fast conversion of the primary species to $HOBr$ (Wachsmuth et al., 2001). The following checks were made to confirm the chemical identity of the Br isotopes as $HOBr$: Macroscopic amounts of $HOBr$ were produced according to three different methods (Allanic et al., 1997; Dancer, 1863; Koga et al., 1989; Lock et al., 1996; Noszticzius et al., 1982), and the batch controlled by its UV/VIS spectrum (Orlando and Burkholder, 1995). $HOBr$, synthesised in the on-line method described by Koga et al. (1989) was passed at a slow rate over quartz in a thermostated bath. The temperature (203 K) at which $HOBr$ was condensing was consistent with the deposition temperature (188 K) of $HO^A Br$ in the temperature gradient of a thermochromatography experiment (Eichler et al., 1995). Whereas the former is related to the sublimation enthalpy of $HOBr$, the latter is related to the adsorption enthalpy of individual $HO^A Br$ molecules on an inert surface and depends on the gas flow rate and pressure at which the experiment is run (Eichler, 1977; Gäggeler et al., 1986). Any contamination by isotopes in the form of for example HBr that could have been formed due to trace amounts of hydrogen impurities in the carrier gas would have been observed as deposition at much higher temperature, as single HBr molecules are easily absorbed into water adsorbed on any surface.

The system was operated on-line, and steady state concentrations of the bromine isotopes in the flow system were established according to the half-lives of the generating Se isotopes. From the measurement of the count-rates of either the decay precursor selenium or directly the ones of bromine nuclides (Wachsmuth et al., 2001; Wachsmuth et al., 2000), the steady state concentrations of $HO^{83}Br$, $HO^{84}Br$, and $HO^{86}Br$ were 245, 12, and 13 molecules cm^{-3} , respectively. For technical reasons, the decay rate of ^{85}Se could not be measured, but was estimated from the known fis-

sion yield. Br isotopes with masses below 83 or above 86 can be neglected. Summing up, the overall HOBr concentration was about 280 molecules cm^{-3} .

2.2. Generation of deliquescent NaBr aerosols

5 A 0.2 M sodium bromide solution (Fluka 71 329 MicroSelect $\geq 99.5\%$) was nebulised in synthetic air (20% O_2 in N_2 , Sauerstoffwerke Lenzburg) using a homemade nebuliser with a pressure drop of 1.6 bar. The resulting droplets were dried in a diffusion dryer, mounted directly on top of the nebuliser, consisting of a tubular reticule surrounded by silica gel and reducing the relative humidity in the gas to below 5%. Downstream (see Fig. 1), the particles passed an ^{85}Kr source (a bipolar ion source) to establish an
10 equilibrium charge distribution. An electrostatic precipitator removed all charged particles so that only neutral particles were passing on through the experiment to avoid any uncontrollable losses of charged particles in isolating, but chemically inert tubing. The aerosol flow was humidified by passing the gas through an 8 cm long, 0.6 cm i.d., permeable PTFE membrane (Goretex®) tube immersed in water, of which the tem-
15 perature could be controlled. The relative humidity was measured with a capacitance humidity sensor (Rotronic) and could be adjusted to between 20% and 90% at room temperature. For the experiments with the deliquescent particles, it was adjusted to 85%, before this gas flow was admixed to the comparably dry gas containing labelled HOBr.

20 Before the aerosol flow was admitted to the flow tube, a part of it was passing a scanning mobility particle sizer (SMPS), consisting of a ^{85}Kr source, a differential mobility analyser (DMA) and a condensation particle counter (CPC, TSI 3022). During the uptake experiments, the humidity of the sheath air flow in the DMA was adjusted to the same humidity as in the mixed gas of the flow tube so that the size of the deliquescent
25 particles in the DMA was identical to that in the flow tube. The mobility diameter based surface area obtained by this device was used to calculate the gas-kinetic collision rate to the particles.

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2.3. Reaction of labelled HOBr with sodium bromide aerosols

The atmospheric pressure aerosol flow tube was made of perfluoro-alkoxy copolymer (PFA) with an inner diameter of 0.8 cm. The reaction volume and therewith the reaction time could be varied by changing the position of an inner tube ('injector') with an inner diameter of 0.44 cm, also made of PFA, through which the flow containing HOBr ($21 \text{ cm}^3 \text{ s}^{-1}$ STP (standard temperature and pressure) of 5% O_2 in He, $\sim 10\%$ relative humidity) was admitted. To facilitate mixing, the inner tube was plugged, and the gas exited through small holes near the tube end. The aerosol flow ($10.4 \text{ cm}^3 \text{ s}^{-1}$ STP of 20% O_2 in N_2 , 85% relative humidity) entered the reaction tube through a T-connector by passing the annulus formed between the injector and the flow tube walls. In most of the experiments, the relative humidity of the flow tube at room temperature ($23 \pm 2^\circ \text{C}$) was 37%.

The analysis made use of fast isotope exchange between $\text{Br}_{2(\text{aq})}$ and $\text{Br}_{(\text{aq})}^-$ for measuring the uptake to deliquescent particles (see below). Therefore, the main task consisted of separating $\text{HOBr}_{(\text{g})}$ from the particles using a denuder and detecting the activity of the bromine isotopes associated with the coated denuder wall for $\text{HOBr}_{(\text{g})}$ and that associated with the particles retained on a impregnated filter, respectively (see Fig. 2). As the reaction was very fast, a very fast separation was necessary to achieve a reasonable time resolution. A specially developed parallel glass plate denuder with 0.1 cm spacing and 2.6 cm width was used (Ammann, 2001) resulting in a very narrow deposition zone of HOBr and a time resolution of about 10 ms, while the aerosol particles passed with $100\% \pm 5\%$ penetration efficiency as checked using the SMPS system. For an efficient, diffusion controlled absorption of HOBr molecules in the denuder, the glass plates were coated with tetrabutylammonium hydroxide (TBAH, Fluka 86882, pract. $\sim 25\%$ in methanol) (Gandrud and Lazrus, 1983; Sedlacek et al., 1984). The particle filter behind the denuder was a disc of compressed glass fibers (Schleicher & Schuell GF 6) retaining more than 99% of the particles in the submicron size range. The detection of labelled HOBr was restricted to the determination of ^{84}Br and

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⁸⁶Br isotopes, and was realized by γ -spectroscopy using the lines at 881.6 keV and 1564.9 keV, respectively, with a high purity germanium (HPGe) detector (Canberra) mounted to both the denuder plates and the filter. Absolute calibration was performed for both geometries using ⁸⁸Y and ⁵⁴Mn as standard radiation sources. Better counting statistics was obtained when working with ⁸⁴Br; however, due to the half-life of 31.8 min, integration intervals were much longer than with ⁸⁶Br with a half-life of 56 s. Therefore, separate experiments with both nuclides were performed.

For comparison with other experiments on solid bromide surfaces (Mochida et al., 1998) a few experiments were performed under dry conditions with solid NaBr particles (see below). Under these conditions, the isotope exchange is not effective due to the absence of sufficient amounts of aqueous bromide, and uptake of HOBr results in the release of labelled Br₂. For this case, a reasonable separation of HOBr from Br₂ was achieved by mounting an additional denuder in front of the TBAH denuder, which was coated with carbon tetrabromide (CBr₄) (Fluka 86 770, purum) by applying CBr₄, dissolved in carbon disulfide (Merck 102 214, p.a.) to the glass plates. The use of CBr₄ as material to absorb Br₂ has not been reported previously. It was used as low-volatile analogue to CCl₄ in which Br₂ is highly soluble.

3. Results and Discussion

In contrast to pure NaCl (Cziczo and Abbatt, 2000; Luna et al., 1998; Weingartner et al., 1995), the deliquescence and efflorescence properties of the mixed sea salt particles, and also of NaBr, have not been well documented. Malvestuto and Ascoli (2001) estimated the deliquescence humidity of NaBr particles 100 nm in diameter to around 58% from the known activity coefficients. In the present experiment, the humidity in the HOBr flow was kept low to avoid its retention on tube walls before the flow tube. Thus, the final humidity in the flow tube was much lower than in the aerosol flow. Therefore it must be assured that the particles, initially humidified to 85%, remain in their deliquescent state when the humidity is lowered to 37%. First, the humidifier

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in the aerosol flow and in the sheath air flow of the DMA were bypassed to obtain the size of the 'dry' particles at around 6% relative humidity with a modal diameter of 35 nm (Fig. 3). When the humidity in both flows was increased to 37%, adsorption of low amounts of water did not lead to a measurable size change, the particles did clearly not deliquesce. When the humidity was increased to 85% (for both aerosol and DMA sheath air) the particles got deliquescent and increased their size accordingly. When, by dilution with the carrier gas of the HOBr flow, after the particles equilibrated at 85%, the humidity was decreasing to 37% again, the particles reduced their size, but remained clearly deliquescent, and did not shrink to the dry size. Thus, under the conditions adopted below for most experiments at 37% relative humidity, the particles were supersaturated bromide solutions.

A few experiments were performed with dry particles. The interaction time in the flow tube was adjusted to 3.27 s, and the relative humidity was 6% at room temperature. First, the aerosol was switched off, and the activity associated with absorption of HO⁸⁴Br on the TBAH denuder was measured. Retention of HOBr on CBr₄ led also to a significant signal on the first denuder (Fig. 2). As the flow of ⁸⁴Br was not always constant due to variations in the neutron source, all measured activities are reported in normalised form. Typical counting rates measured at the detector were between 0.2 and 1.0 s⁻¹, with a detection limit of 0.1 s⁻¹, for both isotopes. After "switching on" the aerosol (by opening the supply of bromide solution to the nebuliser), all ⁸⁴Br activity was associated with the CBr₄ denuder, clearly indicating complete conversion of HO⁸⁴Br to ⁸⁴BrBr. It also demonstrates the ability of the relatively unpolar CBr₄ to retain Br₂ and to only weakly interact with HOBr. Br₂ would also be efficiently absorbed by TBAH (Sedlacek et al., 1984). Based on a few more experiments not shown here, and the total aerosol surface area in the flow tube of $1.10 \times 10^{-4} \text{ cm}^2 \text{ cm}^{-3}$, an uptake coefficient, γ_{upt} , of at least 0.5 was estimated. This is still higher than the value observed by Mochida et al. (1998) at the lowest concentration. At 6% relative humidity, adsorption of water at defect sites of the crystalline NaBr surface may already lead to partial solvation of bromide available for reaction (1). Indications of ionic species on

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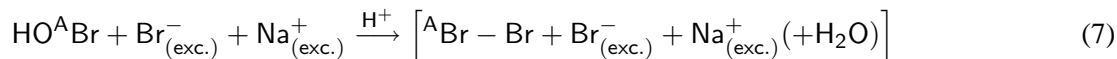
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NaCl surfaces were found based on spectroscopic evidence (Beichert and Finlayson-Pitts, 1996) and on results of the reaction with HNO_3 (Davies and Cox, 1998) far below the deliquescence humidity of NaCl. Whether under these conditions the NaBr substrate can provide the acidity necessary for reaction (1) as in the case of an aqueous solution, remains an open question.

More detailed kinetic experiments were performed with deliquescent particles in the flow tube at 37% relative humidity and room temperature. Again, for a reaction time of 0.90 s, first the steady state activities at the denuders and the filter were observed while no aerosol particles were present (see Fig. 2). When then the aerosol was “switched on”, the activity on the filter increased while that on the denuders decreased to below detection limits, clearly indicating complete uptake of $\text{HO}^{\text{A}}\text{Br}$ into the particles. Fast isotope exchange between Br_2 and aqueous bromide keeps the $^{\text{A}}\text{Br}$ isotope as bromide in solution and results in activity on the particle filter, and non-labelled Br_2 is released:



The kinetics of the analogous isotope exchange between Cl_2 in halogenide solutions was studied by Long and Olson (1936) and reported by Wahl and Bonner (1951). This isotope exchange is due to the equilibrium



with an equilibrium constant of 16.1 M^{-1} (Liu and Margerum, 2001), and forward and reverse rate constants are $5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $5 \times 10^7 \text{ s}^{-1}$, respectively (Ruasse et al., 1986). Therefore, in a saturated bromide solution (48.6% wt. = 4.72 M (Lide, 1998)), the characteristic time for exchange was much faster than that of separation of gas-phase Br_2 from the particles (10^{-3} s) or even than that of diffusion out of the liquid particle (10^{-5} s , estimated from d_p^2 / D_{aq}). Thus, each $^{\text{A}}\text{Br}$ detected on the particles

has gone through the complete reaction in the aqueous phase of the deliquescent particles. When the γ -detector for HO^ABr was placed further downstream along the denuder plate, no signal from ^ABr was observed indicating that not a significant fraction of labelled HOBr or Br₂ was slowly desorbing from the particles on the time scale of a few tens of milliseconds after the main part of HOBr(g) has been removed from the gas phase.

As we could not observe the few non-labelled Br₂ molecules on the CBr₄ denuder, for all other experiments described below, the CBr₄ denuder was omitted to improve the time resolution and the counting statistics for HO^ABr on the TBAH denuder. Figure 4 shows the result of a number of experiments at different reaction times, showing the decrease of activity at the TBAH denuder associated with HOBr_(g), and the increase of activity on the particle filter associated with reacted HOBr. The average aerosol surface to volume ratio was $1.25 \times 10^{-3} \text{ cm}^2 \text{ cm}^{-3}$. For each data point a reference experiment without aerosol was performed, in which the counting rate at the denuder downstream of the flow tube was compared with that measured when the flow tube was bypassed, to check for losses of HO^ABr on the flow tube walls due to deposition of particles. In the latter case, the PFA tube was exchanged. A new PFA tube did not show any detectable loss or retention of HO^ABr.

The net first order loss rate of HOBr_(g) derived from a fit to the data shown in Fig. 4 was 4.2 s^{-1} resulting in a γ_{net} of 0.53 (Eq. (3)). For such high net uptake, a small correction for diffusion according to Eq. (4) might be adequate even though the particles were small. As the diffusion coefficient of HOBr in the gas-mixture of the flow tube, composed of He, O₂, N₂ and H₂O, was not readily available, the diffusion was calculated from the diffusion coefficients of each binary mixture:

$$\frac{1}{D_{\text{tot}}} = \frac{p_{\text{He}}}{D_{\text{He}}^{\text{HOBr}}} + \frac{p_{\text{O}_2}}{D_{\text{O}_2}^{\text{HOBr}}} + \frac{p_{\text{N}_2}}{D_{\text{N}_2}^{\text{HOBr}}} + \frac{p_{\text{H}_2\text{O}}}{D_{\text{H}_2\text{O}}^{\text{HOBr}}} \quad (10)$$

resulting in $D_{\text{tot}} = 0.263 \text{ cm}^2 \text{ s}^{-1}$. p_X is the partial pressure of X [Torr] and D_X^{HOBr} the diffusion coefficient of HOBr in X [$\text{Torr cm}^2 \text{ s}^{-1}$]. The D_X^{HOBr} were estimated according to

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the first approximation reported by Hirschfelder et al. (1954) for the diffusion coefficient of gas 1 in gas 2:

$$[D_{12}]_{1.\text{approx.}} = 2.628 \cdot 10^{-3} \frac{\sqrt{T^3(M_1 + M_2) / 2 M_1 M_2}}{p \sigma_{12}^2 \Omega_{12}^{(1,1)*} [T_{12}^*]}, \text{ in cm}^2 \text{ s}^{-1} \quad (11)$$

where T is temperature [K], M_1 is molecular mass of HOBr and M_2 of the transport gas component, p is the pressure [atm], σ_{12} is the average of the collision diameters of the corresponding molecule pair (Abbatt, 2001; Hirschfelder et al., 1954; Lide, 1998), and Ω is a tabulated function of the Lennard-Jones potential (Hirschfelder et al., 1954). For He, N₂, and H₂O these values for $D_{\text{He}}^{\text{HOBr}}$, $D_{\text{N}_2}^{\text{HOBr}}$ and $D_{\text{H}_2\text{O}}^{\text{HOBr}}$ are comparable with those measured by Fickert et al. (1999). Based on the diffusion coefficient obtained here and Eq. (4), $1/\Gamma_{\text{diff}}$ was 0.071. Therefore, the uptake coefficient, γ_{upt} , becomes 0.55, which already indicates that uptake might have been accommodation limited. Whether the resistance to reaction in the liquid phase limited the uptake is mainly determined by the first order loss rate in the liquid phase due to the equilibrium reaction (1), with forward and reverse rate constants $1.6 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$ and 110 s^{-1} , respectively (Eigen and Kustin, 1962). The major uncertainty with assessing this rate is the H⁺ concentration in the deliquescent particles under our experimental conditions. The pK_a of the cation acid (Na⁺) is 14.8 (Lide, 1998) and the pK_b of the anion base (Br⁻) is ~20 (Schröter et al., 1994), from which we would expect that the NaBr solution should be acidic. A saturated solution of NaBr prepared in our laboratory had a pH of around 3 when measured with a pH probe (Metrohm E-510) in Millipore water. Using this value and the bromide activity ($\alpha_{\text{NaBr}(\text{sat})} = 0.56 - 0.57$ (Resnik et al., 1984)) we estimated the H⁺ concentration to about 1.75 mM. Due to reaction with the very few HOBr molecules, the [H⁺] concentration was not depleted during reaction. Therefore, we expect the equilibrium for (1) to be far on the right side:

$$\frac{[\text{Br}_2]}{[\text{HOBr}]} = 1.2 \cdot 10^6, \quad (12)$$

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and the first order loss rate k_{aq}^I becomes about 10^8 s^{-1} . This leads to a value of 1.2×10^{-3} for $1/\Gamma_{rxn}$ according to Eq. (6), which is not a significant contribution to $1/\gamma_{upt}$, even when an uncertainty of two orders of magnitude in k_{aq}^I is assumed. The reacto-diffusive length, i.e., the characteristic distance beyond the surface after which the HOBr has been lost due to reaction, is on the order of 10^{-7} cm , indicating that under the assumed conditions, HOBr mostly reacted close to the surface. The concentration of HOBr was so low that at most one HOBr molecule was processed per particle, so that H^+ was never depleted. We conclude that under our experimental conditions, uptake was limited by an accommodation coefficient, α , of about 0.6. In Fig. 4, the thin lines indicate the calculated uptake for an uptake coefficient of 1 and 0.3, respectively, setting the limits within which the experimental data lie. Allowing the diffusion coefficient varying by 30% would lead to values for γ_{upt} between 0.54 and 0.56. The main error associated with this experiment is coming from estimating the surface area based on the measurements using the SMPS system. Whereas the diameter can be determined to within better than 5% relative error, a significant error can be induced by non-ideal counting efficiency of the CPC, or by a few particles outside the size range covered by the DMA. Allowing the total aerosol surface area varying by 30%, the γ_{upt} values derived from the fit to the data as shown in Fig. 4 would range from 0.42 to 0.80. Therefore, it seems realistic to report the accommodation coefficient as 0.6 ± 0.2 , and our result confirms the expectations by Fickert et al. (1999) and Abbatt and Waschewsky (1998).

The theoretical uncertainty associated with this derivation is related to the parameterization used in Eq. (6), which assumes that the loss to the surface is due to the reaction in the bulk liquid phase. The present experiment does not allow to find evidence for a surface specific reaction which would extend Eq. (6) by a pathway leading from a weakly bound, not dissolved, molecule on the surface directly to Br_2 (see Hanson (1997) for a description of the extended parameterisation). Such surface processes on liquids have been proposed for, e.g., Br_2 , Cl_2 and BrCl (Hu et al., 1995; Katrib et al., 2001). In addition, the present approach does not allow to separate the accom-

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modation coefficient into the primary sticking probability, S , i.e., the probability that the molecule is not reflected upon collision, and the rate of solvation (Hanson (1997), and references therein). However, recent molecular dynamics simulations of the uptake of molecules into aqueous solutions (Taylor et al., 1997; Wilson and Pohorille, 1997) indicate that the accommodation coefficient might often be close to 1 mainly because the excess kinetic energy is easily dissipated into the water and a significant free energy barrier of solvation is lacking, so that hydration of the molecule can occur extremely rapidly. Therefore, whatever the fate of HOBr is in detail, HOBr lost from the gas phase seems to have undergone hydration, i.e., accommodation, before reaction to Br_2 .

4. Atmospheric implications

We used the box model MOCCA to estimate the effects of a change of α_{HOBr} by a factor of 10 because in older versions of MOCCA (Sander and Crutzen, 1996; Vogt et al., 1996) α_{HOBr} was estimated to be 0.056. We assume that the accommodation coefficient measured here also holds for a deliquescent sea salt solution. The model treats reactions in the gas and aerosol phase explicitly with a special emphasis on the halogen chemistry in the marine boundary layer. A very comprehensive reaction set is used for sulphate and sea salt aerosols and the coupling of aerosol chemistry with the gas phase. For information on the updated version of the box model MOCCA that is used here see <http://www.mpch-mainz.mpg.de/~sander/mocca>.

We studied the impact of a factor of 10 in the accommodation coefficient for HOBr in two scenarios. In the first scenario strong bromine activation from the sea salt aerosol takes place, about 95% of the initial Br^- is released to the gas phase. In the second scenario only a moderate bromine activation occurs with a release of about 50%.

In both scenarios an increase of α_{HOBr} leads to lower concentrations of O_3 , but the reasons are different. In the strong activation scenario, an increase in the uptake of HOBr does not lead to a significant increase in bromine release from the sea salt aerosol, because it already is mainly partitioned to the gas phase. Br_x , the sum of

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all reactive inorganic gas phase bromine species except HBr, does not change significantly. The change in α_{HOBr} does, however, lead to an increase in chlorine release from the sea salt aerosol via the reaction



- 5 and therefore to an increase in Cl_x (sum of all reactive inorganic gas phase chlorine species except HCl). These Cl_x species (mainly ClO and Cl) are responsible for an increase in O_3 loss in this scenario. The initial bromine release from the sea salt aerosol is slowed down a bit in the model run with lower α_{HOBr} (see Fig. 5a).

10 In the modest activation scenario a higher α_{HOBr} does lead to additional release of bromine from the sea salt aerosol. With $\alpha_{\text{HOBr}} = 0.06$, about 43% of the bromine is released to the gas phase, whereas with $\alpha_{\text{HOBr}} = 0.6$, about 57% are lost from the sea salt aerosol. In this scenario both Cl_x and Br_x increase in the gas phase when α_{HOBr} is increased from 0.06 to 0.6 and radicals of both halogens are responsible for the stronger loss of O_3 (see Fig. 5b).

15 5. Conclusions

Due to the complexity of the experiment and the limited availability of the large facilities involved, only a limited dataset on the uptake of HOBr to deliquescent NaBr aerosol was obtained. Nevertheless, quantitative results were obtained that are, when using conventional experimental methods, only hardly or even not at all accessible. From the experiments presented here, the accommodation coefficient of HOBr on deliquescent NaBr was 0.6 ± 0.2 , which is consistent with the limits set by previous estimates and also adds to current thinking of very high accommodation coefficients of soluble gases on aqueous solution. This is one order of magnitude higher than that used in modeling studies of the marine boundary layer (Sander and Crutzen, 1996; Vogt et al., 1996).

25 The model calculations show that the effect of the increased accommodation coefficient on the marine boundary layer is by slightly increasing the ozone loss and quite

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significantly increasing chlorine release.

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References

- Abbatt, J. P. D.: Heterogeneous reaction of HOBr with HBr and HCl on ice surfaces at 228 K, *Geophys. Res. Lett.*, 21, 665–668, 1994.
- Abbatt, J. P. D.: Personal Communication, 2001.
- Abbatt, J. P. D. and Waschewsky, G. C. G.: Heterogeneous interactions of HOBr, HNO₃, O₃, and NO₂ with deliquescent NaCl aerosols at room temperature, *J. Phys. Chem. A*, 102, 3719–3725, 1998.
- Allanic, A., Oppliger, R., and Rossi, M. J.: Real-time kinetics of the uptake of HOBr and BrONO₂ and in the presence of HCl in the temperature range 190–200 K, *J. Geophys. Res.*, 102, 23 529–23 541, 1997.
- Ammann, M.: Using ¹³N as tracer in heterogeneous atmospheric chemistry experiments, *Radiochim. Acta*, in press, 2001.
- Ammann, M., Kalberer, K., Jost, D. T., Tobler, L., Rössler, E., Piguet, D., Gäggener, H. W., and Baltensperger, U.: Heterogeneous production of nitrous acid on soot in polluted air masses, *Nature*, 395, 157–160, 1998.
- Arens, F., Gutzwiller, L., Baltensperger, U., Gäggener, H. W., and Ammann, M.: Heterogeneous reaction of NO₂ on diesel soot particles, *Environ. Sci. and Technol.*, 35, 2191–2199, 2001.
- Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., and Rasmussen, R. A.: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, *Nature*, 334, 138–141, 1988.
- Barrie, L. A., den Hartog, G., Bottenheim, J. W., and Landsberger, S.: Anthropogenic aerosols and gases in the lower troposphere at alert Canada in April 1986, *J. Atmos. Chem.*, 9, 101–127, 1989.
- Beichert, P. and Finlayson-Pitts, B. J.: Knudsen cell studies of the uptake of gaseous HNO₃ and

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- other oxides of nitrogen on solid NaCl: The role of surface-adsorbed water, *J. Phys. Chem.*, 100, 15 218–15 228, 1996.
- Blatchley, E. R., III, Johnson, R. W., Alleman, J. E., and McCoy, W. F.: Effective Henry's law constant for free chlorine and free bromine, *Wat. Res.*, 26, 99–106, 1992.
- 5 Bottenheim, J. W., Barrie, L. A., Atlas, E., Heidt, L. E., Niki, H., Rasmussen, R. A., and Shepson, P. B.: Depletion of lower tropospheric ozone during Arctic spring: The Polar Sunrise Experiment 1988, *J. Geophys. Res.*, 95, 18 555–18 568, 1990.
- Bottenheim, J. W., Gallant, A. G., and Brice, K. A.: Measurements of NO_γ species and O_3 at 82 degrees N latitude, *Geophys. Res. Lett.*, 13, 113–116, 1986.
- 10 Cziczo, D. J. and Abbatt, J. P. D.: Infrared observations of the response of NaCl, MgCl_2 , NH_4HSO_4 , and NH_4NO_3 aerosols to changes in relative humidity from 298 to 238 K, *J. Phys. Chem. A*, 104, 2038–2047, 2000.
- Dancer, W.: Über die unterbromige Säure, *Liebig's Ann. Chem.*, 125, 237–249, 1863.
- Davies, J. A. and Cox, R. A.: Kinetics of the heterogeneous reaction of HNO_3 with NaCl: Effect of water vapor, *J. Phys. Chem. A*, 102, 7631–7642, 1998.
- 15 Eichler, B.: Behaviour of volatile radionuclides in a tube with temperature gradient in vacuum, Zentralinstitut für Kernforschung, Rossendorf, 1977.
- Eichler, B., Baltensperger, U., Ammann, M., Jost, D. J., Gäggeler, H. W., and Türlér, A.: Thermochromatographic investigation on ^{13}N labeled nitrous gases and of fission noble gases at low temperatures, *Radiochim. Acta*, 68, 41–49, 1995.
- 20 Eigen, M. and Kustin, K. J.: The kinetics of halogen hydrolysis, *J. Am. Chem. Soc.*, 84, 1355–1361, 1962.
- Fan, S.-M. and Jacob, D. J.: Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols, *Nature*, 359, 522–524, 1992.
- 25 Fickert, S., Adams, J. W., and Crowley, J. N.: Activation of Br_2 and BrCl via uptake of HOBr onto aqueous salt solutions, *J. Geophys. Res.*, 104, 23 719–23 727, 1999.
- Finlayson-Pitts, B. J., Livingston, F. E., and Berko, H. N.: Ozone destruction and bromine photochemistry at ground level in the Arctic spring, *Nature*, 343, 622–625, 1990.
- Frenzel, A., Scheer, V., Sikorski, R., George, C., Behnke, W., and Zetzsch, C.: Heterogeneous interconversion reactions of BrNO_2 , ClNO_2 , Br_2 , and Cl_2 , *J. Phys. Chem. A*, 102, 1329–1337, 1998.
- 30 Fuchs, N. A. and Sutugin, A. G.: Highly dispersed aerosols. Ann Arbor Science Publishers, Inc., Ann Arbor, London, 1970.

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- Gäggeler, H. W., Eichler, B., Greulich, N., Trautmann, N., and Herrmann, G.: Vacuum-thermochromatography of carrier-free species, *Radiochim. Acta*, 40(3), 137–143, 1986.
- Galbally, I. E., Bentley, S. T., and Meyer, C. P.: Mid-latitude marine boundary-layer ozone destruction at visible sunrise observed at Cape Grim, Tasmania, 41 degrees S, *Geophys. Res. Lett.*, 27, 3841–3844, 2000.
- Galbally, I. E. and Roy, C. R.: Destruction of ozone at the earth's surface, *Q. J. R. Meteorol. Soc.*, 106, 599–620, 1980.
- Gandrud, B. W. and Lazrus, A. L.: Preparation of tetrabutylammonium hydroxide for atmospheric sampling of acidic halogen gases, *Anal. Chem.*, 55, 988–989, 1983.
- Hanson, D. R.: Surface specific reactions on liquids, *J. Phys. Chem. B*, 101, 4998–5001, 1997.
- Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric acid aerosols: a framework for model calculations, *J. Geophys. Res.*, 99, 3615–3629, 1994.
- Hausmann, M. and Platt, U.: Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, 99, 25 399–25 413, 1994.
- Hebestreit, K., Stutz, J., Rosen, D., Matveiv, V., Peleg, M., Luria, M., Platt, U., Oltmans, S. J., and Komhyr, W. D.: DOAS measurements of tropospheric bromine oxide in mid-latitudes, *Science*, 283, 55–57, 1999.
- Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B.: *Molecular theory of gases and liquids*. John Wiley & Sons, Inc., New York, London, Sydney, 1954.
- Hu, J. H., Shi, Q., Davidovits, P., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E.: Reactive uptake of $\text{Cl}_2(\text{g})$ and $\text{Br}_2(\text{g})$ by aqueous surfaces as a function of Br^- and I^- ion concentration: the effect of chemical reaction at the interface, *J. Phys. Chem.*, 99, 8768–8776, 1995.
- Kalberer, M., Ammann, M., Arens, F., Gäggeler, H. W., and Baltensperger, U.: Heterogeneous formation of nitrous acid (HONO) on soot aerosol particles, *J. Geophys. Res.*, 104, 13 825–13 832, 1999.
- Kalberer, M., Tabor, K., Ammann, M., Parrat, Y., Weingartner, E., Piguet, D., Rössler, E., Jost, D. T., Türler, A., Gäggeler, H. W., and Baltensperger, U.: Heterogeneous chemical processing of $^{13}\text{NO}_2$ by monodisperse carbon aerosols at very low concentrations, *J. Phys. Chem.*, 100, 15 487–15 493, 1996.
- Katrib, Y., Deiber, G., Schweitzer, F., Mirabel, P., and George, C.: Chemical transformation of bromine chloride at the air/water interface, *J. Aerosol Sci.*, 32, 893–911, 2001.
- Kirchner, U., Benter, T., Schindler, R. N., Hirokawa, J., Onaka, K., Kajii, Y., and Akimoto, H.:

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- Experimental verification of gas phase bromine enrichment in reactions of HOBr with sea salt doped ice surfaces, *Ber. Bunsenges. Phys. Chem.*, 101, 975–977, 1997.
- Koga, Y., Takeo, H., Kondo, S., Sugie, M., Matsumura, C., McRae, G. A., and Cohen, E. A.: The rotational spectra, molecular structure, dipole moment, and hyperfine constants of HOBr and DOBr, *J. Mol. Spectr.*, 138, 467–481, 1989.
- Langendörfer, U., Lehrer, E., Wagenbach, D., and Platt, U.: Observation of filterable bromine variabilities during Arctic tropospheric ozone depletion events in high (1 hour) time resolution, *J. Atmos. Chem.*, 34, 39–54, 1999.
- Le Bras, G. and Platt, U.: A possible mechanism for combined chlorine and bromine catalyzed destruction of tropospheric ozone in the Arctic, *Geophys. Res. Lett.*, 22, 599–602, 1995.
- Lide, D. R.: *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1998.
- Liu, Q. and Margerum, D. W.: Equilibrium and kinetics of bromine chloride hydrolysis, *Environ. Sci. Technol.*, 35, 1127–1133, 2001.
- Lock, M., Barnes, R. J., and Sinha, A.: Near-threshold photodissociation dynamics of HOBr: Determination of product state distribution, vector correlation, and heat of formation, *J. Phys. Chem.*, 100, 7972–7980, 1996.
- Long, F. and Olson, A.: The rate of exchange between chloride ion and chlorine in aqueous solution, *J. Am. Chem. Soc.*, 58, 2214, 1936.
- Luna, M., Rieutord, F., Melman, N. A., Dai, Q., and Salmeron, M.: Adsorption of water on alkali halide surfaces studied by scanning polarization force microscopy, *J. Phys. Chem. A*, 102, 6793–6800, 1998.
- Malvestuto, V. and Ascoli, S.: A deliquescence model for alkali halide nuclei, *Meteorol. Z.*, 10, 37–43, 2001.
- McConnell, J. C., Henderson, G. S., Barrie, L., Bottenheim, J., Niki, H., Langford, C. H., and Templeton, E. M. J.: Photochemical bromine production implicated in Arctic boundary- layer ozone depletion, *Nature*, 355, 150–152, 1992.
- Mickle, R. E.: Boundary layer ozone depletion during AGASP-II, *Atmos. Environ.*, 23, 2443–2449, 1989.
- Mochida, M., Akimoto, H., van den Bergh, H., and Rossi, M. J.: Heterogeneous kinetics of the uptake of HOBr on solid alkali metal halides at ambient temperature, *J. Phys. Chem. A*, 102, 4819–4828, 1998.
- Mozurkewich, M.: Mechanisms for the release of halogens from sea-salt particles by free radi-

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- cal reactions, *J. Geophys. Res.*, 100, 14 199–14207, 1995.
- Nagao, I., Matsumoto, K., and Tanaka, H.: Sunrise ozone destruction found in the sub-tropical marine boundary layer, *Geophys. Res. Lett.*, 26, 3377–3380, 1999.
- Noszticzius, Z., Noszticzius, E., and Schelly, Z. A.: On the use of ion-selective electrodes for monitoring oscillating reactions 1. potential response of the silver halide membrane electrodes to hypohalous acids, *J. Am. Chem. Soc.*, 104, 6194–6199, 1982.
- Oltmans, S. J.: Surface ozone measurements in clean air, *J. Geophys. Res.*, 86, 1174–1180, 1981.
- Oltmans, S. J. and Komhyr, W. D.: Surface ozone distributions and variations from 1973–84 measurements at the NOAA Geophysical Monitoring for Climatic Change baseline observatories, *J. Geophys. Res.*, 91, 5229–5236, 1986.
- Orlando, J. J. and Burkholder, J. B.: Gas-Phase UV/Visible Absorption Spectra of HOBr and Br₂O, *J. Phys. Chem.*, 99, 1143–1150, 1995.
- Resnik, S. L., Favetto, G., Chirife, J., and Fontan, C. F.: A world survey of water activity of selected saturated salt solutions used as standards at 25°C., *J. Food Sci.*, 49, 510–513, 1984.
- Ruasse, M.-F., Aubard, J., Galland, B., and Adenier, A.: Kinetic study of the fast halogen-trihalide ion equilibria in protic media by the Raman-laser temperature-jump technique. A non-diffusion-controlled ion-molecule reaction, *J. Phys. Chem.*, 90, 4382–4388, 1986.
- Sander, R. and Crutzen, P. J.: Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea, *J. Geophys. Res.*, 101, 9121–9138, 1996.
- Schröter, W., Lautenschläger, K.-H., and Bibrack, H.: Taschenbuch der Chemie. Harry Deutsch, Thun, Frankfurt am Main, 1994.
- Sedlacek, W. A., Lazrus, A. L., and Gandrud, B. W.: Measurements of stratospheric bromine, *J. Geophys. Res.*, 89, 4821–4825, 1984.
- Stutz, J., Hebestreit, K., Alicke, B., and Platt, U.: Chemistry of halogen oxides in the troposphere: Comparison of model calculations with recent field data, *J. Atmos. Chem.*, 34, 65–85, 1999.
- Tang, T. and McConnell, J. C.: Autocatalytic release of bromine from Arctic snow pack during polar sunrise, *Geophys. Res. Lett.*, 23, 2633–2636, 1996.
- Taylor, R. S., Ray, D., and Garrett, B. C.: Understanding the mechanism for the mass accommodation of ethanol by a water droplet, *J. Phys. Chem. B*, 101, 5473–5476, 1997.
- Tuckermann, M., Ackermann, R., Golz, C., Lorenzen-Schmidt, H., Senne, T., Stutz, J., Trost, B., Unold, W., and Platt, U.: DOAS-observation of halogen radical-catalysed arctic bound-

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- ary layer ozone destruction during the ARCTOC-campaigns 1995 and 1996 in Ny-Alesund, Spitsbergen, Tellus, 49B, 533–555, 1997.
- Vogt, R., Crutzen, P. J., and Sander, R.: A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature*, 383, 327–330, 1996.
- 5 Von Glasow, R., Sander, R., Bott, A., and Crutzen, P. J.: Modeling halogen chemistry in the marine boundary layer. 1. Cloud-free MBL, *J. Geophys. Res.*, submitted, 2001.
- Wachsmuth, M., Eichler, B., Tobler, L., Hänssler, F., Gäggeler, H. W., and Ammann, M.: Chemical characterisation of short-lived selenium nuclides from thermal neutron induced fission of ^{235}U at a gas-jet facility, *J. Radioanal. Nucl. Chem.*, submitted, 2001.
- 10 Wachsmuth, M., Eichler, B., Tobler, L., Jost, D. T., Gäggeler, H. W., and Ammann, M.: On-line gas-phase separation of short-lived bromine nuclides from precursor selenium, *Radiochimica Acta*, 88, 873–877, 2000.
- Wahl, A. C. and Bonner, N. A.: *Radioactivity applied to Chemistry*. John Wiley & Sons, Inc., New York, 1951.
- 15 Weingartner, E., Baltensperger, U., and Burtscher, H.: Growth and structural change of combustion aerosols at high relative humidity, *Environ. Sci. Technol.*, 29, 2982–2986, 1995.
- Wessel, S., Aoki, S., Winkler, P., Weller, R., Herber, A., Gernandt, H., and Schrems, O.: Tropospheric ozone depletion in polar regions – A comparison of observations in the Arctic and Antarctic, *Tellus*, 50B, 34–50, 1998.
- 20 Wilson, M. A. and Pohorille, A.: Adsorption and solvation of ethanol at the water liquid-vapor interface: A molecular dynamics study, *J. Phys. Chem. B*, 101, 3130–3135, 1997.

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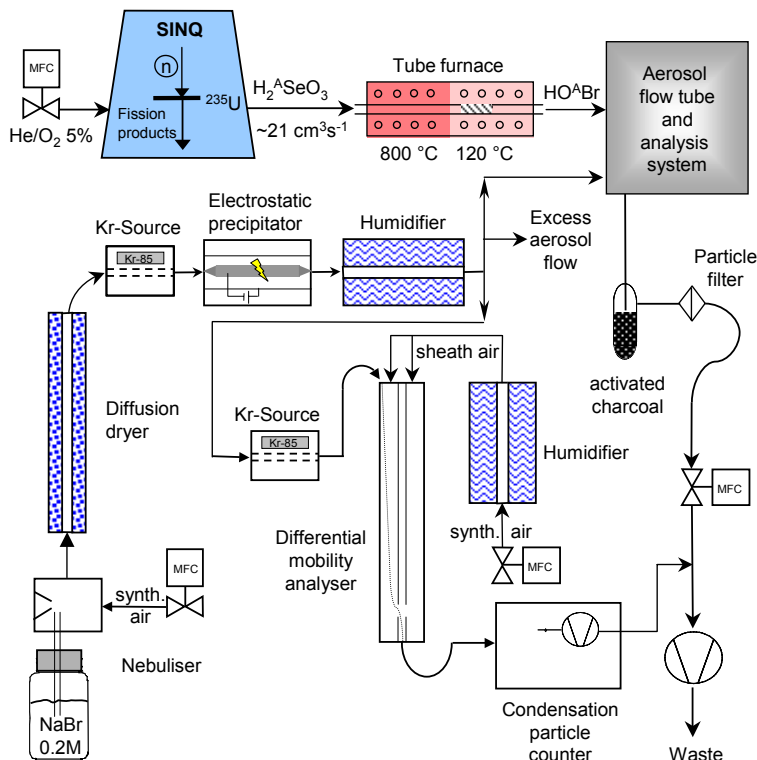


Fig. 1. Set-up of the on-line HO^{18}Br source and the NaBr aerosol generator, coupled together to measure uptake of HOBr on the aerosol in flow tube experiments. Mass flow controllers are denoted by MFC, for further details see text.

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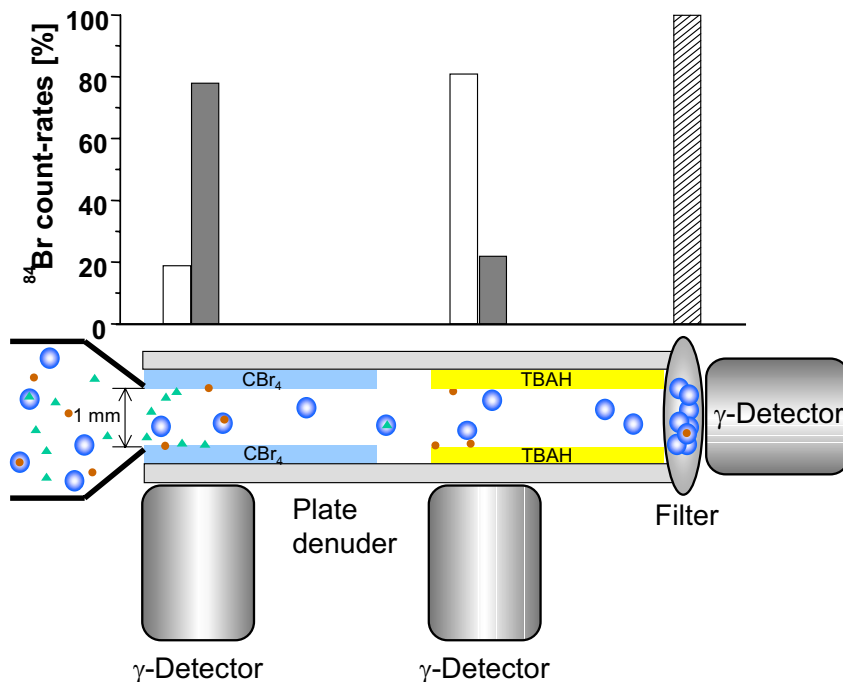


Fig. 2. Analytical set-up for the determination of Br count-rates associated with $\text{HOBr}_{(\text{g})}$, $\text{Br}_{2(\text{g})}$ and the aerosol, consisting of a portable γ -detector that can be placed at the denuder system adjacent to the plates coated with CBr_4 and TBAH to absorb $\text{Br}_{2(\text{g})}$ and $\text{HOBr}_{(\text{g})}$, respectively, or at an impregnated filter, respectively. The bars indicate the normalised count-rates measured by the detector and corrected for counting efficiency (empty bars: in absence of NaBr aerosol particles; grey bars: in presence of dry NaBr particles; hatched bar: in presence of deliquescent NaBr particles) for experiments with 3.3 s (dry case) and 0.9 s (deliquescent case) reaction time.

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**Accommodation
coefficient of HOBr**

M. Wachsmuth et al.

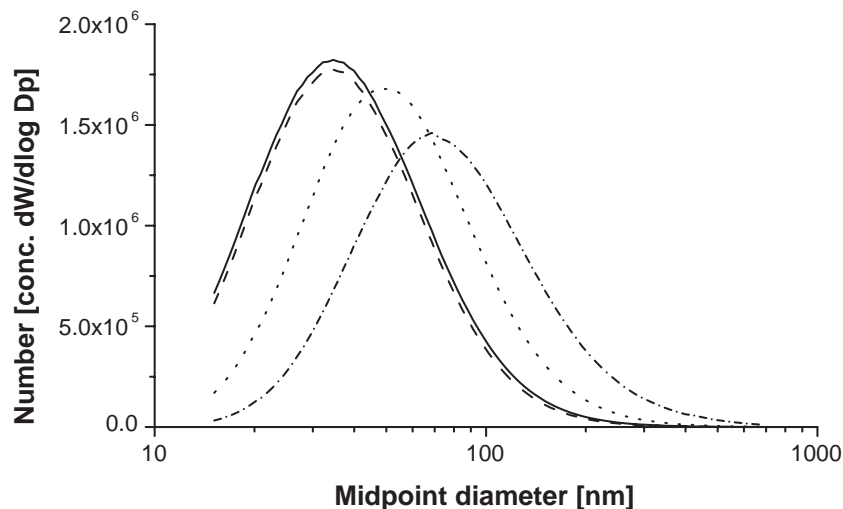


Fig. 3. The change of the number size distribution with humidity for dry and deliquescent NaBr particles. At 6% r.h. a modal diameter of 35 nm results (solid line), which not measurably changes after increasing the humidity to 37% (dashed line). Deliquescence is obviously reached at 85% r.h. (dash dotted line) and remains after decreasing the humidity again to 37% (dotted line). Due to varying losses in these different configurations, the number concentrations are not matching.

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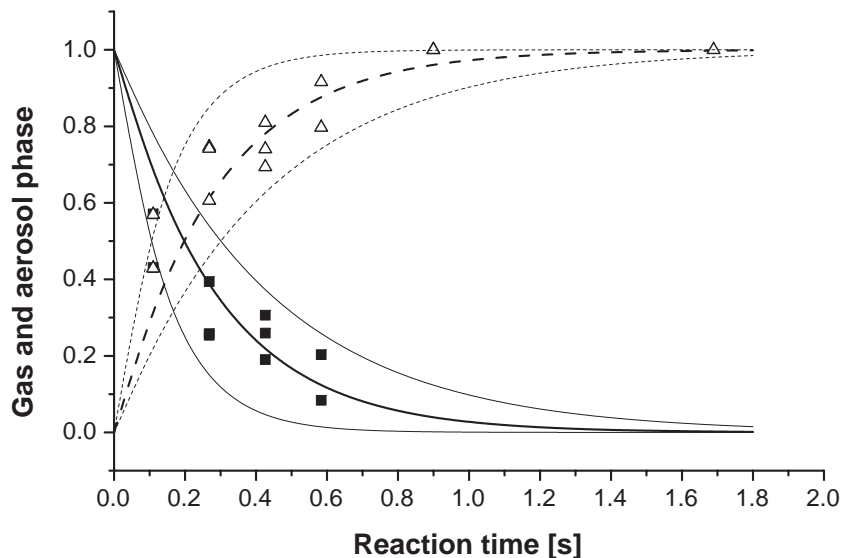


Fig. 4. Uptake of HOBr to deliquescent NaBr particles for reaction times in the range of 0.1 to 1.7 s. With increasing reaction time, the Br activity on the particles increases (open triangle), which is measured on the filter. The activity associated with HOBr(g) decreases with increasing reaction time (plain squares). The bold lines (solid: $\text{HO}^{\text{A}}\text{Br}(\text{g})$, dashed: $^{\text{A}}\text{Br}^{-}(\text{aq})$) are a fit of a mass transfer calculation based on the formalism explained in the text to the experimental data. The thin lines are the corresponding curves for γ_{upt} of 0.3 and 1.0, for reference.

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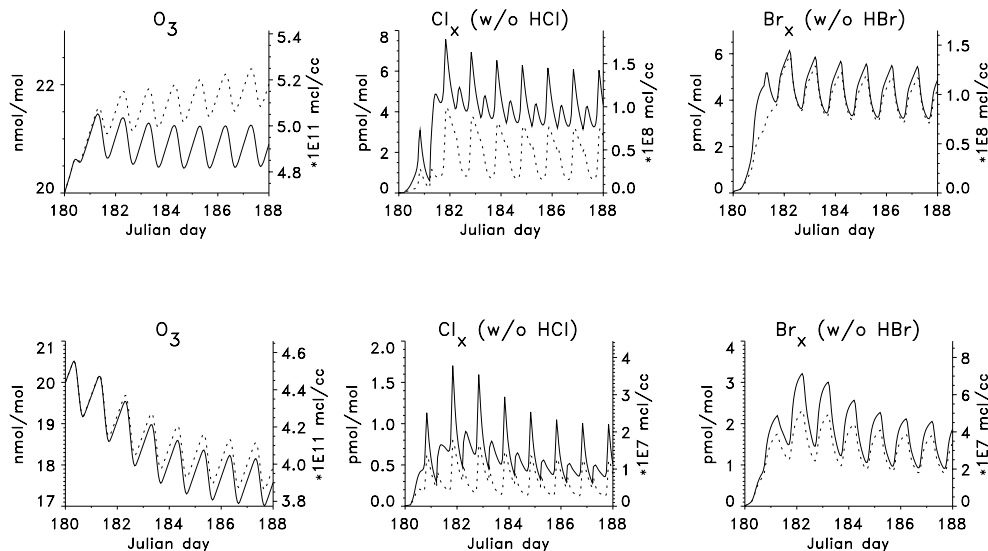


Fig. 5. Results of model runs using the MOCCA box model for the marine boundary layer. Evolution with time of O_3 , Cl_x and Br_x (sum of all reactive inorganic gas phase chlorine/bromine species except HCl/HBr) for a scenario with strong bromine activation (a) and moderate bromine activation (b). The solid line is for the cases with $\alpha_{\text{HOBr}} = 0.6$ and the dashed line for $\alpha_{\text{HOBr}} = 0.06$. Note the different scales on the plots.

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